

Report of the IADN Technical Review Panel (12/5/97)

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Executive Summary:

The review panel finds that IADN (Integrated Atmospheric Deposition Network) is a strongly successful binational program especially considering the relatively modest resources allocated. Viewed from a global perspective, IADN is a leading international effort in the assessment of the role of the atmospheric impacts of persistent, toxic substances on aquatic systems. It has largely been successful in addressing objectives of the GLWQA and Annex 15 and initial goals of the CAA Section 112. It is critical that the IADN be continued in a consistent but evolutionary and improved fashion to provide the long-term record of toxic chemical concentrations in the atmosphere and loadings to the Great Lakes. Results from IADN demonstrate the importance of the atmosphere both as a source (via precipitation, gas absorption and dryfall) and sink (via volatilization from water and terrestrial surfaces) for contaminants. The IADN monitoring results have also demonstrated for the first time that air concentrations of PCBs and other persistent organochlorines are declining significantly in the Great Lakes region. Back trajectory modelling with IADN data has shown the importance of sources within the basin (metals, PAHs) and long distances away (toxaphene, DDT). Although the scientific output of IADN, in terms of peer-reviewed papers, is impressive it is also uneven; one or two principal investigators account for almost all publications. IADN has failed to address all of the original goals set out in GLWQA Annex 15 and CAA Section 112 especially the issues of atmospheric loadings “relative to other pathways”, the determination of “movement or transformation of toxic substances”, and source identification and transport across and into the basin. There is a discontinuity between operations and strategy of the network and its goal to obtain the best estimates of loadings. Reducing the large uncertainty of loadings estimates will require increased harmonization of timing of sampling, and of analytical methodology (media and species). Improved estimates of loadings will also require research to improve understanding of processes such as air-water exchange, atmospheric degradation, air-vegetation and air-soil interactions. Managers of the IADN program should find ways of stimulating this essential research either by IADN investigators or other

experts. The interlab quality assurance program, which demonstrated reasonable agreement between participants for most analytes early on in the program, needs to be re-established by the appointment of a QA manager and development of a pro-active program including exchange of standards and matrices. More attention should be given to communicating IADN results and implications of those results to the scientific community, media, and the public.

Recommendations:

1. Strong attention should be paid to the continuity issue of the IADN operational network and analytical protocols so that comparability of the data is maintained as the program evolves.
2. Air monitoring stations should be established in a representative number of major urban areas along the lakes. (e.g., Chicago, Toronto or possibly Detroit/Windsor). Criteria for siting in a locally-contaminated urban environment should be developed.
3. A QA Manager and Data Manager for IADN should be hired as soon as possible. This will re-establish a pro-active QA program including exchange of standards and matrices. The QA program should also include sampling, such as the side-by-side sampler operations at Point Petre, to ensure comparability results among participating agencies.
4. IADN activities should be harmonized (samplers, frequency, duration, analytical procedures, parameters) to the maximum extent possible. Failure to do this will compromise the credibility of loading estimates and other conclusions drawn from the network.
5. IADN monitoring site(s) should be established over the water off major urban area(s) and off rural areas in order that data is available on shore-based over land and over-water concentration differences.
6. Chemicals measured in air at IADN stations should be measured in nearby waters during the same time frame to reduce uncertainty in future loadings estimates.
7. Criteria should be established to evaluate which chemicals are analyzed. Examples are: detected in current program, chemical-physical properties; production and use history; persistence and bioaccumulation; connection to the Northern Contaminants program; watershed vs lake interactions; analytical and collection feasibility; human health concern; problem chemicals noted in other international monitoring or research efforts. The reasons for selecting a chemical should be well documented. It is a concern that IADN will become

irrelevant if the flexibility to add new or presently-unknown chemicals is not included.

8. Continue to extend the IADN activities to support and add value by developing explicit collaborations with other research programs (AEOLUS, Northern Contaminants Program, LMMB; PAMS in terms of siting characteristics).
9. Introduce modeling components for source identification, loading estimations and scenario analysis. The long term goal should be to construct a coupled lake-atmosphere model.
10. Use the IADN database to apply source models and source-receptor modeling strategies to assess in-basin and out-of-basin sources and impacts.
11. Support research in support of IADN activities to improve understanding of the processes influencing loading estimates and source identification: physical-chemical constants; isotopic analyses; air-vegetation and air-soil interactions; mass transfer coefficients for air-water exchange; atmospheric degradation pathways, mechanisms and rate constants; single particle analysis (e.g. by time-of-flight mass spectrometry).
12. More attention should be given to communicating IADN results and implications to the scientific community, media, and the public. Examples: EOS and ES&T feature articles; documentaries; enhanced Web page; pamphlets for State agencies and public; press releases.
13. Research should be conducted in support of the basin-wide toxics strategy to determine the atmospheric contribution to tributary loadings.

The Review Panel's Response to Steering Committee Questions on the Implementation of IP1:

1. Did IADN do what it said it would do in IP1?

a. Did IADN meet the goals for monitoring and surveillance set out in the Great Lakes Water Quality Agreement Annex 15. Where are the shortfalls against the mandate? What are the successes?

Overall, IADN has met its basic goals and furthermore has had a major scientific impact through several high profile, well documented papers in peer reviewed journals (e.g. Hoff et al. 1996; Hillary et al. 1997). There is no other international program of monitoring for persistent organic pollutants or heavy metals that is as detailed, as long term, or as successful in meeting its original goals.

Short falls: Annex 15 calls for investigating the significance of atmospheric inputs “relative to other pathways.” However, information on other pathways is limited for most Great Lakes so that this comparison cannot be made. Tributary inputs could be quite significant depending on watershed-lake area ratios (gas absorbed SVOCs) and extent of urban runoff (PAH, metals). Sources (Annex 15 iiC2) contributing to atmospheric inputs within the basin or outside the basin have only been investigated on a qualitative basis using on data from Egbert and Pt Petre. There seems to have been no attempt to do this systematically by taking advantage of multiple simultaneous measurements.

There has been little progress in modeling (Annex 15, 2c) to “determine movement or transformation of toxic substances.” Measurements of SVOCs and PAHs have focussed on readily measured components and not on atmospheric transformation products i.e. products of reactions with OH radical. Some effort has gone into estimating deposition velocities which are critical to dry deposition estimates (Hoff and Brice 1993). But the modelling approaches used, i.e. two-film theory for gas exchange and Junge/Pankow estimates for particle sorption, are not new or highly original. Furthermore the mass balance modeling leaves out several important pathways (e.g. tributaries) and processes (fog, spray) because of lack of information.

There are a limited number of satellite stations, especially on the US side, and there is evidence of

lack of compatibility of these sites (convenience of opportunity rather than plan). The satellite stations are not well positioned in terms of geographical coverage of the Great Lakes basin. There is overrepresentation in the Lake Erie/Ontario region because the majority (8 of 14) are in southwestern Ontario. Given that there is “less spatial variability than originally expected .. (p. 22)” the repositioning of some satellite stations should be considered. The stations should be classified better. Are all necessary? Can they be subdivided into background, rural, semirural, according to surroundings and source areas?

Regional contaminant “signals” are adequately covered by the Master Stations for priority toxic chemicals but little attention is given by IADN to source identification and transport across and into the basin. The question of in-basin and out-of-basin emission and transport, is still outstanding.

Annex 15 calls for investigating atmospheric inputs “relative” to other inputs. There is limited activity (IADN and otherwise) to determine the other inputs. This would seem to be in contradiction to the major goal of IADN to satisfy Annex 15 and the CAA. Who is assessing other loadings (tributary, urban runoff, other discharges) of these same chemicals on IADN list? Modeling of sources and deposition have not yet been obvious activities of IADN but with the availability of a large database from Phase 1 should be more important in IADN Phase 2.

Successes: The IADN has become **the** template for the implementation of the national air toxics deposition effort (e.g., Chesapeake Bay, Gulf of Mexico, New Jersey). The understanding of gas absorption inputs and volatilization losses of SVOCs, PAHs and metals has been advanced very significantly as a result of the increased amount of data made available from IADN, and the efforts of individual scientists in the program to interpret that data (e.g. Hoff et al. 1996; Hillery et al. 1997 in press).

There has been a significant effort to evaluate uncertainties in the modeling (e.g. Hoff 1994; Hoff et al. 1996) and measurements (QA programs). The evaluation of errors associated with air-water gas exchange calculations is particularly valuable for focussing future research efforts.

b. Did IADN meet the goals for monitoring and surveillance set out in the CAA Section 112? Where are the shortfalls against the mandate? What are the successes?

Shortfalls: As noted for Annex 15, the “relative contribution” of atmospheric inputs cannot be accurately assessed because information on other pathways is limited for most Great Lakes.

In particular, mercury deposition rates have not been thoroughly assessed yet. Mercury deposition may be an important issue for lakes within the basin, although possibly not for the Great Lakes themselves.

There seems to have been little or no attempt to link IADN results to effects or to consult with those specialists in the “effects” area about their priorities. This is essential for the future because by sticking to a short list of chemicals, most of which have been banned or severely restricted in use in the US and Canada, IADN risks losing its relevance to real world problems. The network should be capable of responding to chemicals of current regulatory interest (e.g. proposed chemicals on the UNECE POPs LRTAP protocol, current use pesticides, endocrine disrupting chemicals such as alkyl phenols) or those most directly associated with effects in Great Lakes biota (dioxins, co-planar PCBs, PCNs).

Major uncertainties in deposition estimates, e.g. lack of simultaneous water measurements near IADN stations, temperature dependence of Henry’s Law constants, deposition velocities in urban vs remote sites, have been identified but not addressed by additional research. IADN lacks a mechanism to directly stimulate/fund this kind of investigation.

Successes: See above for Annex 15 comments.

c. Has IADN’s progress been adequate? What is a reasonable rate and mechanism of delivery of this type of information to the scientific community, to policy makers, and to the public?

Considering the success at achieving the initial goals IADN may be one of the best kept secrets in the field of atmospheric monitoring of toxics. IADN has had a major scientific impact through several high profile, well documented papers in peer reviewed journals (e.g. Hoff et al. 1996; Hillary et al. 1997). There are also numerous internal technical reports. PIs have also made numerous presentations on their work. Overall, this rate of delivery is about right and quite

comparable to other programs on persistent chemicals, e.g. Northern Contaminants Program in Canada, AEOLUS in the US. On the other hand, the report writing and publication writing is a bit uneven; two PIs (Hites and Hoff) account for most of the peer-reviewed output either as senior authors or coauthors.

In quantitative terms the program is a little slow in getting results out. Although results are available back to 1989 or 1990, no data are actually available to the public via a database. The first complete reports on the work were not published until the mid-1990's. Table II-9 shows that some agencies, particularly AES and NWRI are especially slow at getting analytical results completed. In this regard the approach of utilizing graduate students and post-docs to carry out the work and prepare publications seems to work well in terms of fully interpreting the data and getting results out in a timely fashion. The IADN PIs at NWRI, EC Ontario Region and Ontario MOEE may want to consider collaborative work with some of the Canadian University groups who could help interpret and report their results.

The mechanism of delivery, i.e. peer reviewed publications in high profile journals such as ES&T is the most appropriate outlet for influencing scientists and science managers. Results from IADN will be directly useful in the Binational Strategy for Virtual Elimination of Toxic Substances (1997). It is unclear from the technical report whether IADN has had any impact on policy makers. Presumably the declines in persistent organics are good news for policy makers but the mechanism by which this information is passed to them is not clear. It is also unclear whether the public is aware of the key findings of IADN, i.e. that atmospheric inputs are important and that inputs to the lakes of toxics to the lakes are declining. A section in the Technical Report on the interactions of IADN PIs with the media and participation at public meetings would be useful in the report. IADN may want to involve the media, policy advisors and ENGOs in future activities such as updating parameter lists.

Results from the IADN and their implications ("The Great Lakes Air Toxics Story") need to be told. Possible outlets are feature articles in ES&T, EOS, video documentaries, newspaper features, conferences and workshops. Get the word out in any form to the stakeholders. Data

accessibility to the larger community should be a priority. There is a pressing need for the program to have full time QA and Database managers. Rate of overall delivery as well as the quality of results is dependent to a great extent on hiring a QA and Data Manager for IADN.

2. Was the work scientifically credible?

*a. What was the overall **quality** of the research and monitoring being conducted under the IADN program?* The review panel assumed that quality was a combination of scientific credibility developed through interpretation and publication of results, and indicators of good performance of quality control programs for sampling and analysis.

IADN has had a QA program since its inception for both chemical analysis and field sampling. Uncertainties in the analysis of all major parameters have been examined both within and among labs. The analytical variation reported by the QA programs seems to be within an acceptable range. However, there has been no interlab comparison since 1994 because of the loss of the QA manager. Several recommendations of the QA intercomparison such as the use of common analytical reference standards, have not been followed up. Results of studies on co-location of samplers have not been fully interpreted or reported. The Review Panel heard that the results from side-by-side samplers were comparable, but no results were presented. These results really need to be reported as they are an important piece of QA information for tying the whole network together.

There is no way to fully answer this question of quality of the monitoring until the side-by-side sampling/analysis results are made available.

The review committee agrees with the need (outlined in p.86 of the Technical Report) for updating of the QAPP and the use of Quarterly audits. To fulfill these QA tasks there is a critical need for a QA Manager. The review committee also recommends the use of common reference standards for all major analytes and well as the preparation of control samples that are analysed by each laboratory regularly.

The perceived quality of IADN results also comes from publications. A very good record of publication has now been established. PIs have published, submitted or had accepted at least 17

papers in peer reviewed scientific journals over the past 5 years that are directly related to IADN measurements. However, this publication record is uneven; some PIs have not yet prepared papers for peer-reviewed journals. The publication record also appears to be uncoordinated across the basin. More of the SVOC data from the US Stations has been interpreted and published (e.g. Hillery et al. 1997a,b) than from Canadian Master and satellite stations. The IADN steering committee needs to consider ways of encouraging the timely preparation of scientific publications as part of its communication strategy.

b. Are the findings of the loads and trends credible?

The effort to estimate loadings with available data has been very good to date with two major publications. IADN PIs are at the forefront of the science of estimating loadings from gas exchange and dry deposition. However, the review committee foresees problems in refining these estimates in the future. There is a discontinuity between the operations and strategy of the network and its goal to obtain the best estimates or least uncertainty of loading (esp. dry deposition; air-water exchange; urban influence, physical-chemical constants). The uncertainty in the loadings, exemplified by Hoff et al. (1996) and Hillery et al. (1997) may be great especially in air-water exchange fluxes and dry particle deposition. However, even the timing of sampling and actual analyses (media and species) require harmonization so that estimates may be improved.

Consider dry deposition of target chemicals. The estimate requires the concentration of the chemical in the settling particle and size- and composition-differentiated particle characteristics which must be extrapolated over time and space to obtain whole-lake annual loadings. Presently, one part of the network composites the filters collected every 12 days into a monthly sample, another composites the filter and adsorbent, and the other does not analyze the filter at all. This strategy, along with the frequency of sampling (24 hours each 12th day), limits the ability to assess dry deposition. Assuming a $V_d = 0.2$ cm/s assumes dry particle deposition is dominated by sub-micron particles. Chemically-dependent particle size distributions are rare if available at all. The PAH and PCB size distributions coming out of the AEOLUS project show important concentrations in both the sub- and super-micron size regime, especially in the urban areas. Combined with the apparent importance of dry deposition of large particles in and near urban/industrial centers suggests that loading estimates may be underestimated.

Consider air-water exchange of target chemicals. K_{ol} is driven by wind speed and characteristics of the chemicals. The most rigorous approach is to estimate K_{ol} values from the distributions of wind speeds and temperatures over the whole lake for the whole year. It is especially important to develop the wind speed probability distributions. The actual model selected for air-water exchange is unimportant if K_{ol} values empirically determined from tracer experiments (e.g., SF₆) are used. Additionally, linked air-water measurements should be the goal of the network, or at least to evaluate the seasonal changes in air concentrations linked to seasonally-dependent water concentrations. The data coming from the LMMB project should be helpful. It is likely that air-water exchange fluxes as presently estimated are also underestimated. In summary, to reduce the uncertainties in atmospheric chemical fluxes, it is recommended that each component of the calculation model should be evaluated relative to the implementation of the IADN with respect to each component of sample collection and analysis.

The observation of declining concentrations of SVOCs in air at US stations is an important finding. No explanation is given for the lack of a trend at Eagle Harbor. The observation of similar atmospheric trends in half-lives for compounds with much different properties and sources, e.g. DDT and HCB is difficult to understand. Committee members were a bit skeptical about the comparison (Table II-10) of the “half-lives” of PCBs in the technical report. In most cases these so-called half-lives are actually residence times or disappearance times because they are due to multiple pathways and processes.

c. How does IADN compare against the quality and standards of international networks to monitor and assess the deposition of POPs and heavy metals?

The program compares very favorably with international efforts on both POPs and metals for monitoring networks. As far as review committee members are aware there is no program for SVOCs in air which has operated for as long a period of time as IADN. The coordination of activities (QA, database, publications) among IADN participants is much better than similar other international efforts (e.g. Arctic Monitoring and Assessment Program, North Sea Program). While the Quality Assurance program was well planned and implemented initially, it cannot now be

considered as rigorous as other monitoring networks because there has been no interlab comparison since 1994. The reliance of IADN only on internal lab QA to assure quality is not acceptable in the long term especially with changes in PIs and other personnel.

3. Was the work technically sound? Were the timing, monitoring and analysis techniques, network design, etc. adequate?

Overall the quality of the analytical techniques is very good based on the QA results. The laboratories of IADN PIs are among the leading analytical labs in this field in Canada and the US. The quality is especially good on SVOC gases where good agreement was obtained between co-located samples. The agreement is not very good on SVOC particles due to the differences in handling the particle phase among labs. The original design of IADN was adequate to define the regional signal. Future design changes must address the new information documenting the importance of urban sources.

Less is known about the quality of the sampling/monitoring since we do not have the intercomparison results for side-by-side sampling.

Sampling and analysis protocols differ considerably between labs for both air and precipitation. While interlab comparison and co-location of samplers provides assurance of intercomparability of specific results, the different frequency of sampling for organics in precipitation (14 d vs 28 day vs monthly) and for metals in air (12 d vs 28 d for different time periods) may present problems in terms of comparison of loadings estimates and trend evaluation. Differing analytical protocols for metals (extraction and quantitation) present interpretation problems.

The shift to 1 in 12 day sample resolution, and the decision by AES to forego analysis of filters, may be justified in the case of organochlorines but could pose problems in the future if IADN expands its list of analytes to include, for e.g. less volatile pesticides like atrazine, or planar PCBs and dioxin/furans. USGS monitoring using Eagle harbour, has shown atrazine to be present mainly on particles. The use of 12 day frequency for determining gas phase loadings of current use pesticides which, according to USGS data, have a relatively narrow window of elevated

concentrations, could cause great underestimation of loadings of these compounds.

4. *Based on new scientific knowledge, were the right questions asked in IP1 or did more important scientific questions go unanswered? Were IADN's priorities correctly placed? Were the right measurements being made? Were the right chemicals being measured?*

Overall, the right questions were asked in IP1. The goals set out in 1990 reflect the state of knowledge at that time. As noted above, the first published results from IADN (1996-97) have had, and are having, a significant scientific impact. IADN is viewed as an example of the state-of-the-art in monitoring of POPs and heavy metals in air and in estimations of loadings to the aquatic environment. In retrospect IADN placed too much emphasis on regional signals rather than point source, urban signals. The right chemicals were measured although, again in retrospect, perhaps too much emphasis was placed on determining minor PCB congeners versus determining a wider array of organochlorines. The challenge now under IP2 is to refocus IADN with respect to the latest scientific understanding of sources of atmospheric inputs to the Great Lakes while at the same time maintaining continuity of the program.

5. *Does the IP2 correct for our current understanding of the issue or are there still important questions going unanswered which could be addressed by IADN? Does IP2 meet additional information needs?*
- a. *Does IADN contribute to the current and future needs of the scientific community? Does the IP2 improve on IADN's ability to deliver those models? What is missing? What is not necessary?*
- b. *What role could IADN play in meeting additional research needs of Annex 15 and the CAA Section 112? What is missing? What is not necessary?*
- c. *How best can IADN contribute to meeting the objectives of the Binational Toxics Strategy?*

The review committee has reviewed the goals of IP2 given on p. 83 and the recommendations for IP2 on p. 86-90. The Technical report addresses unresolved issues of IP1 (p. 84-85). We concur with these issues and have discussed them above. One area that the recommendations on p. 86-90 does not address directly is the issue of continuity of the network. Strong attention should be paid to the continuity issue of the IADN operational network and analytical protocols so that

comparability of the data is maintained as the program evolves. The historical record of contaminant levels in air which IADN is recording becomes more valuable with time in terms of addressing binational issues, as a record of global trends in POPs and metals, and as a research database for modelling and understanding air chemistry of semi-volatile pollutants. This requires a significant commitment to intercomparison of analytical methods and sampling techniques. If the data are comparable, there should be no problem with switching to a single collection and analysis methods across the network. However, there seem to be doubts raised about the real viability of their long term record (i.e. pre-1989) for organochlorines in precipitation. The data would be much more credible in terms of their comparability between sites and laboratory if they were to have a single set of unified methods and we believe this is an objective worth working toward.

We agree with most of the comments concerning QC/QA, about larger sampling volumes and the long analysis times. Furthermore, control samples should be developed and distributed to each laboratory and analyzed regularly (e.g. aliquots of the raw extract of a large air sample). We strongly recommend that real simultaneous measurements of air and surface water be carried out over at least 1 year. The experimental determination of important parameters for particle distribution, dry vs. wet deposition should be included if possible. The influence of local sources might be bigger than assumed and we support the proposed by paired/urban remote measurements (eventually semi rural in addition to gain more significance). The use of enantioselective methods should be included for selected organochlorines at least in selected samples due to its power to detect the direction of fluxes.

A re-evaluation should be carried out of the chemicals that are currently determined in the existing program. Those which give the same type of information can then omitted. This would allow others to be included without increasing the work load. For e.g., at least some toxaphene congeners should be included (a further possibility to use enantio-selective separations) as well as herbicides such as atrazine which has been shown to persist in Great Lakes waters. It is a concern that IADN will become irrelevant if the flexibility to add new or presently-unknown chemicals is not included. There are perhaps 1000 compounds identified in Great Lake's atmosphere – and waters. IADN is focussing on only a few although clearly there was a concensus, under IP1 and

GLWQA, about the persistent, bioaccumulative and toxic substances. IADN may want to take a pro-active approach on identification of additional chemicals and elimination of some currently monitored. Criteria should be established to evaluate which chemicals are analyzed: for e.g. detected in current program, chemical-physical properties; production and use history; persistence and bioaccumulation; connection to the Northern Contaminants program; watershed vs lake interactions; analytical and collection feasibility; human health concern; problem chemicals noted in other regional (e.g. LaMPs,) binational (e.g. BGLTS), and international monitoring or research efforts. The reasons for selecting a chemical should be documented to avoid the “list effect” i.e. if it’s on one list it should be on another whatever criteria were used.

Very specifically, we suggest that the list of PCBs and other organochlorines be revisited to eliminate some that are near or below detection limits in most samples. A pared down list might help with speeding up sample analysis. Consideration should be given to use of the best available HRGC methods for separation of PCB congeners. Nearly all can now be separated (Larsen et al. J. Chromatogr. 708, 115, 1995). PCB congener analysis should be standardized for all laboratories to avoid the issue of different numbers of congeners representing total PCB. Detection limits of PCB congeners reported in Tables II-1 and II-2 should be reevaluated – they are quite inconsistent between laboratories. It would be preferable to report them on a concentration basis.

As part of a strategy to detect emerging issues IADN PIs should consider a program of archiving of some samples for future analysis, either as raw extracts or previously analysed samples. The air monitoring work done by the Northern Contaminants Program has included an extract archive. What is the current procedure for storage and archiving of current, already analysed, sample extracts?

Continuing IADN as outlined in the Recommendations for IP2 will meet objectives 1 and 2 of the BGLTS (p. 83). To meet the objective of “continuing research on the atmospheric science of toxic pollutants ...” is a worthy goal but perhaps too ambitious for IADN as currently funded. As the Technical Report notes (p. 84), and this committee has also commented on, IADN has failed to act on the research component of Annex 15 such as air-water exchange monitoring, transport modelling and comparison of relative inputs of contaminants. Some progress has been made on these research-oriented areas as result of individual efforts of IADN PIs.

6. What are the greatest strengths and greatest weaknesses in the IADN program?

IADN's greatest strengths are the geographical and temporal resolution of its database on contaminants in air, the degree of binational cooperation and the quality of the scientific output. IADN has met its basic goals and furthermore has had a major scientific impact through several high profile, well documented papers in peer reviewed journals (e.g. Hoff et al. 1996; Hillary et al. 1997). There is no other international program of monitoring for persistent organic pollutants or heavy metals that is as detailed, as long term, or as successful in meeting its original goals.

Its greatest weaknesses are the limited number of satellite stations, especially on the US side, and the possible lack of compatibility of these sites because convenience of opportunity rather than plan was emphasized. While a strong QA program was set up during the first few years of IADN the current lack of a QA manager to conduct a pro-active program of intercomparisons of analytical methods and sampling procedures among laboratories must also be regarded as a major weakness.

Appendix

Listed below are specific comments on the Review Document from members that were not incorporated into the text. These comments are intended to help clarify the Review document. They do not necessarily reflect the views of all panel members.

- p. 14 and Tables II-1 and II-2. Differences between agencies in MDLs of this magnitude are difficult to understand. The explanation on p. 14 that it is due to sampling demands is not credible.
- p. 16-17. The HRGC for the PCB should be standardized for all laboratories to avoid these different overlaps.
- p. 39, Figure II-3. Reporting of Σ PCB as a variable is problematic given the widely different properties of individual PCB congeners.
- P. 31. It is a good idea to rotate the replication of duplicate air sampling between stations. This would allow detection of major methodological errors.
- P. 40-44. The discussion about the time trends observed at Eagle Harbor (no real change,) and the two other stations is interesting. However, no explanation is given for the different behavior. Have differences in the seasonal maximum/minimum temperatures or the yearly average temperatures been considered as a possible reason (colder region at Eagle Harbor)?
- Table II-11. Despite actual application pattern, distribution and differences in vapor pressure etc. the half lives reported in Table II-11 are about the same. It is difficult to believe that compounds such as DDT and HCB, with such different properties, have the same half lives in the atmosphere. The extensive data transformation (reference temperature) and treatment could hide temporal trends (page 44, line 1). A decline of α -HCH in the Arctic atmosphere could be found directly without problems, why not here?
- p. 45. The conclusions in paragraph 2 on page 45 are rather speculative especially taking the comments in the last paragraph. The data do not really allow to differentiate between banned chemicals and those still in use.
- The list of acronyms is not complete: IDL (page 14, 3rd paragraph, line 6) is missing. MOEE (Table II-4) as well. EC (Table II-6) is missing. TEOMs (page 30) is not included.
- Page 9, 2nd paragraph: The reasoning is not logical. The control programs resulted first in decreasing levels on fish. However, the downward trend levels leveled out due to an unknown reason. Last line: "Chemicals is misleading for two compound classes, a single compound and an element. I do not like the word "chemicals" which is very vague and non-specific. If possible, it should be replaced with compounds, compound classes and/or elements.
- Page 14, line 4: CAAA (not in list of acronyms) or CAA? There is no easily readable table of the primary and secondary target chemicals (not the best word, see before) in the report. Paragraph 4, line 4: This sentence can be misunderstood. Larger volumes allow higher instrumental detection limits. "less demanding" is not clear. Nomenclature should spell "nomenclature" throughout the report.
- The Tables II-1, II-2 and II-3 are difficult to read and interpret. First, the acronyms of the compounds are not explained (worst for PAH). Second, some names are wrong according to the nomenclature (e.g. that for p,p'-DDD). α - and γ -chlordane should be replaced by cis- and trans-chlordane to be consistent with trans-nonachlor etc. as well as with the text (e.g. trans-chlordane is mentioned on page 30). Third, to give detection limits per sample is misleading and not very much informative. They do not tell anything about the detection limit of interest in pg/m^3 or ng/L as listed for the elements (see Table II-4). Detection limit in pg/m^3 or ng/L should be given together with the sample volume plus eventually the final extract volume. This gives the maximum of information. Furthermore, the meaning of A, B and C as well as the embolden numbers is not given in the Table caption of Table II-3. The latter is mentioned in the text but should be repeated here. Table II-4 contains a working recommendation concerning detection limits. This should be included into the other Tables as well.
- Table II-6. Should be altitude rather than "height". Table II-7: The masl (altitude) of the satellite stations is missing (given in Table II-6).
- Page 22/23: The site criteria are first given on page 27. It is referred to them on page 22/23 without making reference to this page (e.g. page 23, line 10,).
- Page 28, line 1: Which site criteria were not met for the Sturgeon Point Station? Please give details. I

agree with the decision to skip the determination of particulate chlorinated organics on the filter. However, some general information about the percentage found on the filter should be given already here (e.g. <5% in average) so that one has not to go to chapter II.3.

- Table II-8: Change some "Hivol" to "HiVol".
- Page 31, line 2: Some summary data about the observed variability for parallel sampling of precipitation should be given. Paragraph 3, line 7: Is it $11 \pm 9\%$ or 9% of 11% ($11 \pm 1\%$)?
- Page 30/31: Newly developed techniques are mentioned but nothing is said about the consequences on future plans and no reference is made to another chapter where this might be discussed. This should be added.
- Page 31: Nothing is said about the major points/content of the QA/QC protocols. This should be briefly mentioned.
- Page 33, 1st dot: No information is given about interlaboratory agreement and intralaboratory variability. 20% relative standards deviation between laboratories is a misleading and wrong expression. 2nd dot: The influence of the solvent on the results is not clear (the word "need" is confusing). A source cannot include a need.
- Page 34, line 4: I cannot see the reason why inorganic analysis is mentioned. The entire sentence is not logical. Last 3 lines before II.1.6: This is very important information that a station audit has been carried out. This should be mentioned earlier in the respective subchapter and a brief summary of the outcome should be given.
- p. 34, line 18-19. The comparison of lab precision and knowledge of air-water exchange processes here seems odd. Perhaps what is meant is that the precision (or uncertainty) of analytical methods is much better than the precision of the estimates of air-water exchange parameters.
- Figure II-2: The seasonal trend of the PCB concentration is easily discerned due to the high concentrations in 1994. The scale should be expanded to 0-600 pg/m³ and data outside the scale indicated by arrows.
- Figure II-3: To show the temperature dependency of such a complex mixture as Σ PCB is not recommendable. First the sum is not defined (which congeners) and the vapor pressure vary widely. Why can one not show this for single congeners as done for the pesticides (page 42, II.2.1.3)? Furthermore, r or r^2 should be added and not only be mentioned in the text. Finally the deviation compared to other data might origin from different congeners included in the sum.
- Page 42, 2nd paragraph, line 3: These long-term changes cannot only be hidden but also directed by temperature effects (not only seasonal but also geographical). Can one really calculate atmospheric half lives from time trends?
- p. 43, last para. The use of the term "pesticides" here is misleading since very few of the chlorinated organics monitored by IADN are currently registered as pesticides in the US or Canada. The term persistent OC pesticides is more precise (but long-winded). Some consideration should be given to redefining terminology of IADN to reflect current regulatory nomenclature.
- Page 47: I feel that the significant decrease of α -HCH in precipitation cannot be observed for air data to the same extend though both media should be in equilibrium. Perhaps this is due to the different presentation. This should be commented and/or air data should be presented in the same way as precipitation (yearly temperature weighted average?) to facilitate a comparison. Why do the precipitation measurements vary so much at Point Petre? Furthermore, one should also show the seasonal variability in the precipitation data as for air. All bars should be given with an estimated or measured error range. Are the changes statistically significant?
- P. 47- 49: The steep decline after 1988/89 at some data set is striking and should be discussed. Is this real? Possible reasons? Artefacts? For dieldrin this decline is the only indication for a decrease which is hardly statistically significant.
- P. 53- 55: Why is only April-December shown? For metolachlor the levels increase in December again. Why? How are the concentrations afterwards? Used quantities should be given in tons to be more in accordance to other lists of usage.
- P. 55, line 2: Why are concentrations with a ">" given? Was the quantification method saturated? Why not precise figures?
- P. 57: The parameters in the loading equations should at least be explained completely. Otherwise it is not possible to understand the meaning of them without the article in Atmos. Environ.
- P. 58: The calculated loadings are based on a number of assumptions. The robustness of the results

and the influence of these estimates on the conclusions presented e.g. in Figure II-11 should be commented on.

- Table II-12 does not contain a comment about #N/A and the units are not repeated on page 60.
- P. 61: Lack of simultaneous measurements of water concentrations are a big problem for the data evaluation so far. Are the data from the literature representative? How much do the water concentrations vary seasonally and over the years? This question must be answered under IP2 to get an impression about the validity of the results in Figure II-11 and Table II-13. The asterisk in Figure II-11 is not explained.
- p. 63, Table II-13. With the net gas emissions of PCBs being so much higher than inputs it is logical to ask what is the source to the water column - can recycling from sediments and watershed inputs account for the balance?
- P. 67, Figure II-12: The net volatilization of DDE for Lake Ontario looks odd. Is this an error in the Figure?
- P. 71, Text: The data for α -HCH and γ -HCH showing the spatial difference are not shown in a Figure. This should be added.
- P. 73, paragraph 2+3: An indication should be made which concentration differences were considered as adequate to a long range transport situation compared to an increase by higher temperature air masses.